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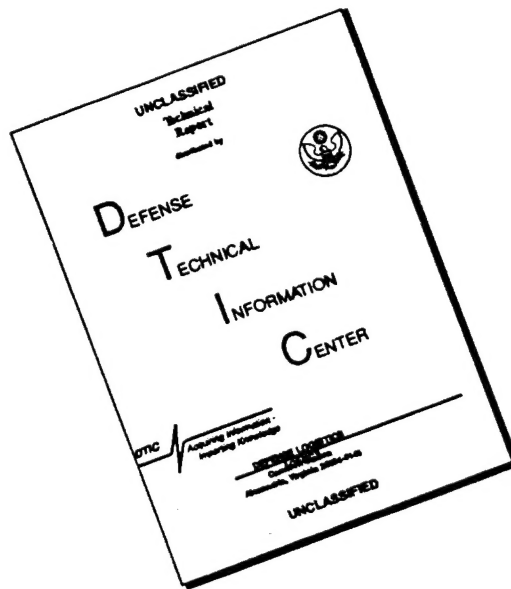
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13. ABSTRACT (Maximum 200 words) Films of amorphous high-Tg azo-containing polymers can be used as reversible optical storage materials. Information can be "written" by inducing orientation with a linearly polarized laser beam and "erased" by restoring disorder with a circularly polarized laser beam. The higher the Tg of the polymer, the higher the stability of the "written" information. One important factor affecting the rate of writing and the level of induced birefringence is cooperative motion of neighboring azo groups, due to dipolar coupling taking place between these groups. Volume holograms can be inscribed by this orientation process, but the efficiency is below 1%. Long exposure times to circularly polarized light produce surface gratings of high efficiency (30% is typical), by a mechanism which involves photoisomerization. Such gratings can be used as coupling elements into a film waveguide. These two phenomena are reported on a carbazole-containing polymer of high Tg (160°C). Asymmetrical two-beam gain coupling in the presence and absence of an electric field is demonstrated, allowing for design of optical switches. In principle, a whole photonic device can be designed on a simple polymer film.					
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Azo-Containing Polymers: Digital and Holographic Storage

by

A. Natansohn and P. Rochon

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polymers for advanced optical applications

Azobenzene-Containing Polymers: Digital and Holographic Storage

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Films of amorphous high-T_g azo-containing polymers can be used as reversible optical storage materials. Information can be "written" by inducing orientation with a linearly polarized laser beam and "erased" by restoring disorder with a circularly polarized laser beam. The higher the T_g of the polymer, the higher the stability of the "written" information. One important factor affecting the rate of writing and the level of induced birefringence is cooperative motion of neighboring azo groups, due to dipolar coupling taking place between these groups. Volume holograms can be inscribed by this orientation process, but the efficiency is below 1%. Long exposure times to circularly polarized light produce surface gratings of high efficiency (30% is typical), by a mechanism which involves photoisomerization. Such gratings can be used as coupling elements into a film waveguide. These two phenomena are reported on a carbazole-containing polymer of high T_g (160° C). Asymmetrical two-beam gain coupling in the presence and absence of an electric field is demonstrated, allowing for design of optical switches. In principle, a whole photonic device can be designed on a simple polymer film.

Azobenzene-containing polymers are reported in the literature at a rate of about 150 papers/year for the last five years. There are two main directions of interest: the first relates to the donor-acceptor substituted azobenzenes as the structure generating second-order polarizability and - by noncentrosymmetrical alignment - second order nonlinear optical properties in "poled" films. The second direction of interest is related to the photoinduced isomerization between the trans (more stable) and cis configurations of the azobenzene. This photoisomerization has a wealth of unexpected and useful consequences which were noted only in the last decade. Both these directions appeared because of the availability of lasers, which on the one hand allowed the observation of the nonlinear optical properties and on the other hand

enhanced the rate of the photochemical isomerization. A review of the recent literature is not within the scope of the present chapter, but some recently published reviews are recommended for general reading on azo polymers¹, nonlinear optical applications², photorefractive properties^{3,4} and liquid crystal alignment using azo compounds^{5,6}.

Research in our laboratory concentrates mainly on the photoisomerization of various azobenzenes bound as side groups in amorphous high-Tg polymers and copolymers. We are also studying the effects of photoisomerization on the orientation of the photoactive groups and on the refractive indices of the random and oriented parts of the polymer film. This paper presents first an overview of the relevant structural factors affecting the orientation process, and then concentrates on two novel findings related to orientation: surface gratings formation and two-beam gain. Their potential applications in photonics are also briefly discussed.

Photoinduced Birefringence in Amorphous Azo Polymer Films: Digital Storage

Linearly polarized light activates the trans-cis photoisomerization of azobenzene groups bound into polymer chain in a selective manner. Since only azobenzene groups having a dipole component along the electric field vector of the light are activated, groups perpendicular to the polarization direction will remain inert and all other groups which happen to fall along the perpendicular direction will become inert. As long as the light is on, the number of azobenzene groups perpendicular to the polarization direction will continuously grow and eventually reach a saturation concentration. This excess number of azobenzene groups perpendicular to the laser polarization direction can be observed as dichroism or as birefringence. When illumination is terminated, there is some relaxation of the photoinduced orientation towards randomization, but the extent of randomization depends significantly on some thermal properties of the polymer film. If the film is amorphous, for example, and has a glass transition temperature (Tg) higher than the operating temperature, a certain amount of oriented azobenzene groups will remain oriented (frozen-in) for an infinitely long time, unless the film is heated to its Tg. This long term photoinduced birefringence is very stable, but can be selectively destroyed by optical means, i.e. by using circularly polarized light. Circularly polarized light will activate **all** azobenzene groups in the plane of the film, with no exclusion for any single direction, which will eventually restore the original randomness of orientation, thus "erasing" the dichroism and birefringence. A typical experiment of inducing, letting it relax and erasing birefringence is shown in Figure 1.

This phenomenon is not new. It had been reported (the photoinduced birefringence part) in amorphous polymer films having azo dyes dissolved in the material⁷. The main disadvantages of using a doped polymer system are the limited loading due to the limited solubility and the intrinsic decrease of the Tg of the material when a small molecule is doped into a polymer. As Tg decreases and comes closer to the operating temperature (usually room temperature), the stability of the photoinduced birefringence starts to vanish. More impetus was generated into this type of research with the advent of liquid crystalline polymers. On a preoriented liquid crystal polymer film, the orientation could be changed by 90° using polarized laser light and generating quite a difference in the refractive indices of the initial and final orientations⁸. The most exciting aspect of the photoinduced birefringence was the

possibility to use it in hologram applications. Interference patterns could be inscribed onto polymer films with excellent contrasts and stability. A significant amount of publications exploiting various aspects of photoinduced birefringence on liquid crystalline polymer films followed, but will not be detailed here.

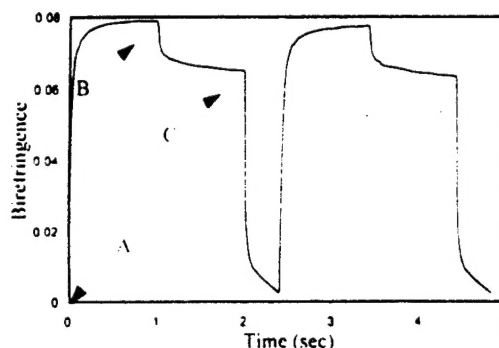


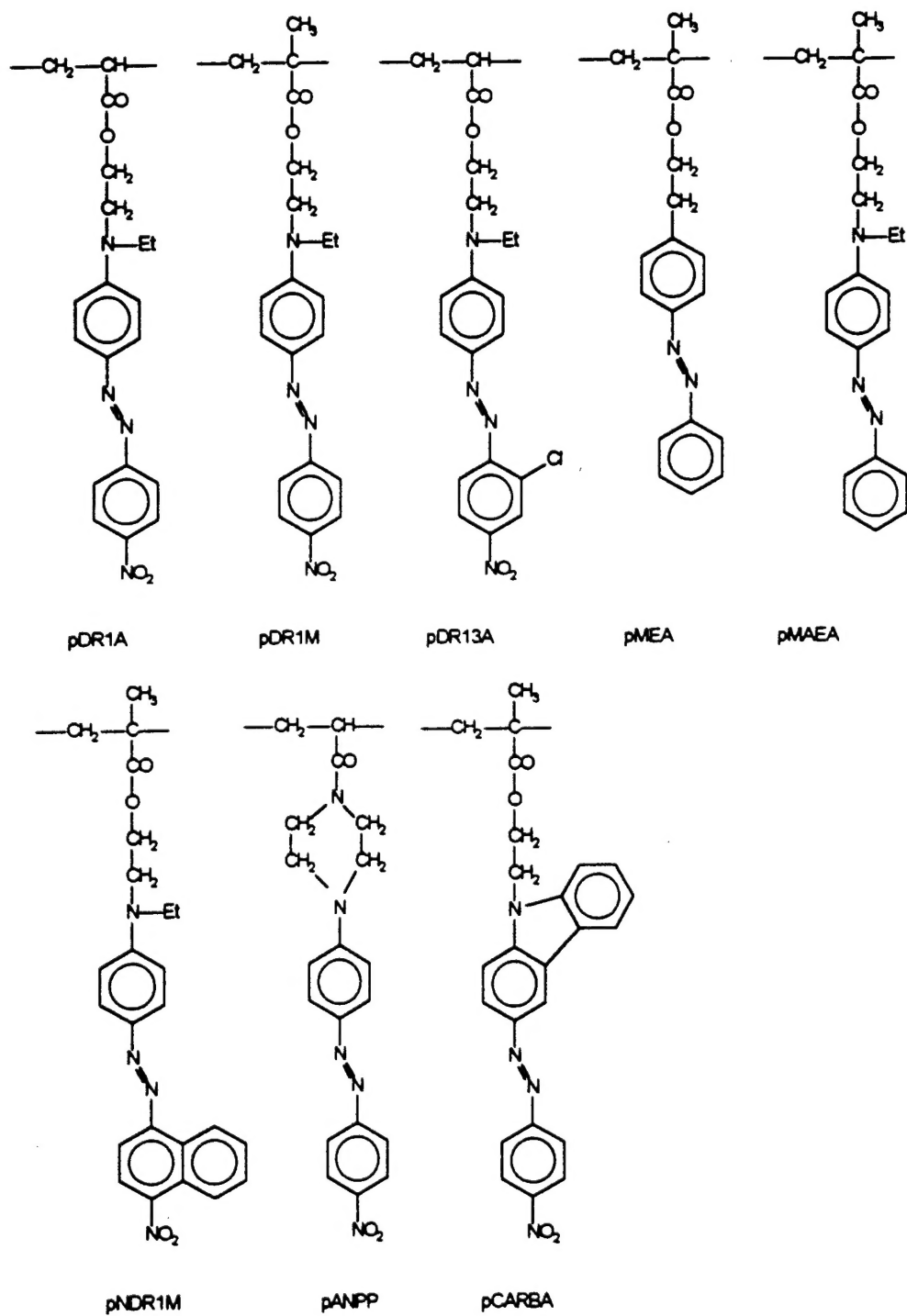
Figure 1. Birefringence is induced (A), it relaxes (B) and is erased (C).

Although most papers investigating such liquid crystalline polymer films had one or two examples of polymers which did not exhibit liquid crystalline phases, but were active in the photoinduced orientation process, the main idea in the literature was that a spacer between the azo group and the main chain was necessary in order to allow the azobenzene group enough freedom to be able to move and achieve the desired orientation. The amorphous polymers investigated in such papers had such spacers, even if they were not long enough to generate liquid crystalline phases.

In fact, contrary to the accepted mechanism at the time, this spacer is not necessary, and the motion of such side groups with short or no spacers was becoming obvious from the study of polymer materials for nonlinear optics. Polymers with higher T_g were proposed and actually used in the poling process, where a polar alignment is achieved with the help of an electric field.

We reported photoinduced orientation on a polymer containing a Disperse Red 1 residue and a very short (2 methylene units) spacer between the azobenzene group and the main chain^{9, 10}. The structure of this first polymer is shown - together with other polymers investigated in our laboratory in Scheme 1.

We regard the photoinduced birefringence as a procedure for digital optical storage. At point A in Figure 1, one "writes" information on the polymer film. Subsequent to point B, the "written" part is conserved for years and can be "read" without affecting it at any time during storage. At point C in Figure 1, "erasing" is being performed, and that specific point on the polymer film is ready for a new cycle of storage. Tens of thousand of "writing/erasing" cycles can be performed on the same point on the polymer film without distortion. After a very long exposure time to the laser, the polymer can eventually degrade. "Writing" a line, instead of a point, on the polymer film, provides an optically-inscribed waveguide, which can be optically "erased" or "re-written". A variety of structural factors affecting the photoinduced orientation phenomenon have been identified.



Scheme 1. Polymers studied in our laboratory (obtained by polymerization)

Structural factors affecting the photoinduced orientation. One obvious important parameter determining the rate and stability of the photoinduced orientation is the glass transition temperature of the polymer film. The higher the T_g , the lower the propensity of the azobenzene groups to move at room temperature, the usual "working" temperature. Thus, for polymers with relatively high T_g one expects a slower rate of the photoinduced birefringence, but also a better stability of the orientation after the light has been turned off. The two structural parameters related to the T_g are the main chain structure and the structure of the spacer or link between the azo group and the main chain. We have not undertaken yet a separate study of these two parameters, so only the analysis of the spacer structure will be shown below.

To describe the growth of the photoinduced birefringence, a biexponential equation can be used as follows¹¹:

$$\Delta n = A[1 - \exp(-k_a t)] + B[1 - \exp(-k_b t)] \quad (1)$$

where k_a and k_b are the rate constants of the two exponential processes and A and B are the weighting coefficients representing the relative contribution of the two processes to the overall birefringence (Δn) growth. In general, the "fast" process is associated with the azobenzene group isomerization and reorientation, while the "slow" process is supposed to involve motional coupling between the azobenzene group and the main chain, as well as any motion of the main chain.

For the relaxation of the photoinduced orientation when the "writing" beam is turned off, a similar biexponential equation can describe the process¹¹:

$$\Delta n = C \exp(-k_c t) + D \exp(-k_d t) + E \quad (2)$$

where k_c and k_d are the rate constants of the two exponential processes, C and D are their weighting coefficients and E is the residual long term birefringence (independent on time). Again, two main processes are assumed to occur and they are associated, as before, with motions of the azobenzene groups (including thermal cis-trans isomerization) and with coupled motions involving the main chain.

The polarity of the azo group. Rau¹² classified azobenzene groups into three categories, according to their isomerization characteristics. The first category, called "azobenzenes" has a relatively slow cis-trans thermal isomerization and consists mainly of groups containing no polar substituents. pMEA, in Scheme 1, belongs to this category. The second category, called "aminoazobenzenes", has a faster cis-trans thermal isomerization rate and, as the name suggests, has amino substituents, which generate larger dipole moments. In Scheme 1, pMAEA belongs to this category. Finally, the third category is called "pseudostilbenes", due to the similarity of isomerization with stilbene molecules, and it typically contains donor-acceptor substituted azobenzene, with large dipole moments. The thermal cis-trans isomerization is very fast in this category, but it is also noteworthy that the trans and

cis absorbances are typically superimposed and the maximum wavelengths lie in the visible range. Most of the other polymers in Scheme 1 belong to this category.

We have studied pMEA, pMAEA and pDR1M in comparison, in order to determine what is the importance of Rau's classification on the photoinduced birefringence¹³. These three polymers have increasing dipole moments, and their comparison clearly indicate that the "pseudostilbene"-type azobenzenes are the best candidates for photoinduced orientation. Their absorbance in the visible range of the spectrum allows the use of lower power lasers (514 nm), the coincidental absorbances of the cis and trans isomers allows photoexcitation of both trans-cis and cis-trans isomerization processes. Both are necessary for orientation, and the lower the polarity of the azobenzene, the slower the cis-trans thermal isomerization process. The levels, rates and stabilities of the photoinduced birefringence, all are higher for pDR1M in comparison with the other two, as is the efficiency of the process. Almost all our research is concentrated on the donor-acceptor substituted azobenzenes.

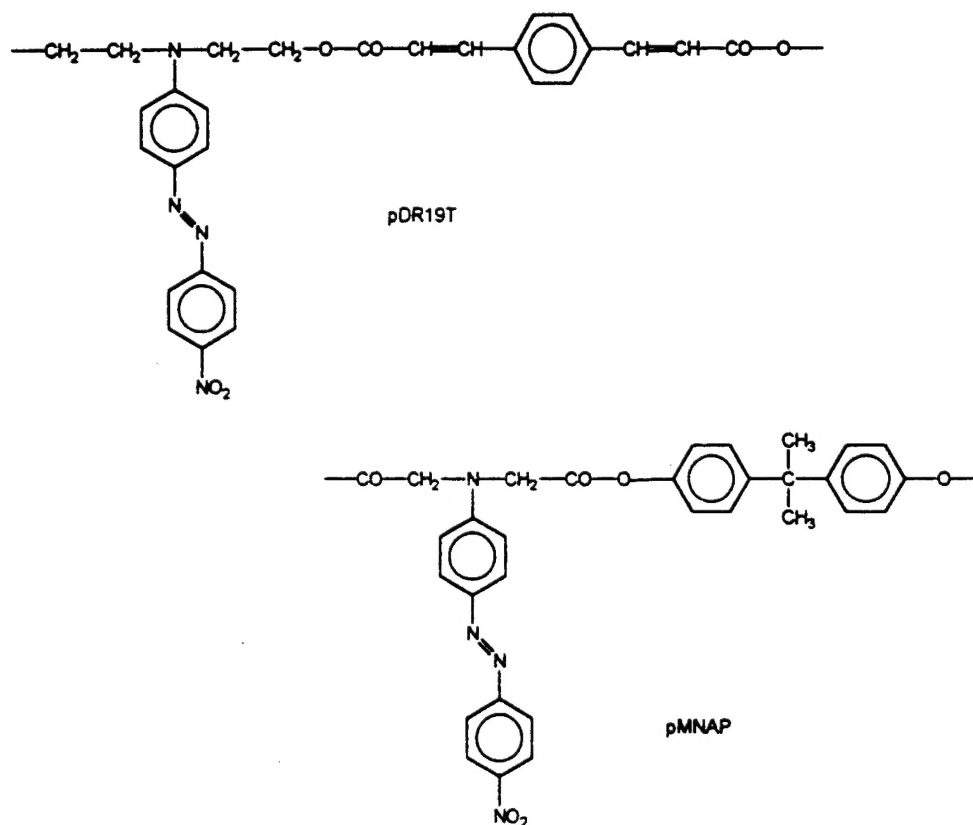
The bulkiness of the azo group. Since isomerization is essential for a photoinduced birefringence, a bulkier azobenzene group, which would require more free volume to isomerize, should be detrimental to the orientation process. This is not the case when one compares the levels of photoinduced birefringence for the bulkier azobenzene investigated by us: pDR13A¹⁴, pNDR1M¹¹ and pCARBA¹⁵, see Scheme 1. The saturation levels of the birefringence are similar or even greater than those achieved in comparable homopolymers (pDR1A compared with pDR13A), due to differences in λ_{max} , but the main differences appear only in the rate by which the birefringence is achieved. A bulkier azobenzene group would take longer to achieve the orientation.

The structure of the spacer between the azo group and the main chain. This parameter affects directly the motion of the azobenzene group, since a rigid link may prevent free motion necessary in achieving orientation. As discussed above, a rigid link would have a double effect: it would require more energy to achieve orientation, but it would also confer a better stability of the orientation, after the light has been switched off. pANPP in Scheme 1 has been compared with pDR1A¹⁶. The two polymers are extremely similar, the main difference in their structures is the spacer (link) between the azobenzene group and the main chain. This spacer is more rigid in pANPP, and although the level of the photoinduced birefringence is similar, the rate of achieving it is much slower for pANPP. As expected, the birefringence is much more stable in pANPP¹⁶. A similar result is obtained for a polymer obtained by polycondensation (pMNAP, shown in Scheme 2¹⁷).

In the case of pMNAP, the azobenzene group is tethered to the main chain by two bonds, and the spacer allowing some motion is much shorter than in all the previously analyzed polymers. Again, due to this structural feature, the Tg of the polymer is much higher, and so are the levels of photoinduced birefringence and its stability in the absence of light.

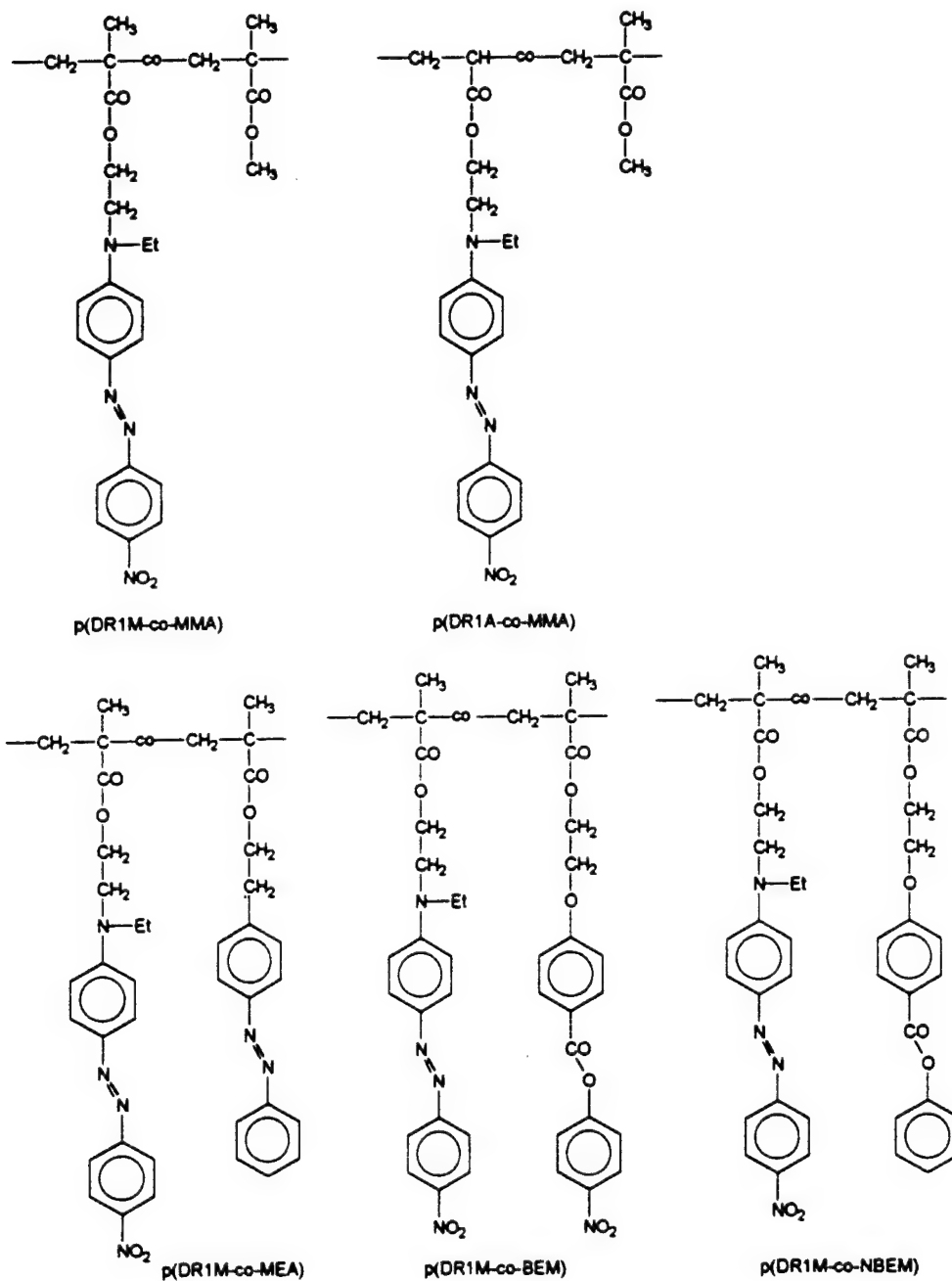
The azo group concentration. The homopolymers shown in Scheme 1 contain one azobenzene group per structural unit. In principle, one would expect a

better orientation if more azobenzene groups are present. To check this assumption, we have investigated a number of copolymers containing azobenzene and "inert" groups, and blends of azobenzene-containing polymers with, for example, poly(methyl methacrylate) (PMMA). This investigation revealed a very intriguing neighboring group effect, thus it was expanded on other copolymers. Blends were not investigated in comparison, since most of the homopolymers were not compatible. Scheme 3 shows the structures of copolymers investigated in our laboratory.



Scheme 2. Polymers studied in our laboratory (obtained by polycondensation)

As expected, the photoinduced birefringence level does depend on the azo concentration, the more azobenzene groups are present in the copolymer, the higher the birefringence level. This is observed for all copolymers¹⁸⁻²¹ but some of the copolymers show a clear deviation from a linear dependence, which has been assigned to a neighboring group effect.



Scheme 3. Copolymers studied in our laboratory

The neighboring group effect. This is an unexpected phenomenon, which is usually common in crystalline and liquid crystalline polymers. If two azobenzene groups are situated close to each other they tend to move in concert. This means that

neighboring groups will be more difficult to reorient, but it also means that after achieving the new orientation they will have a higher tendency to remain in the oriented position than isolated azobenzene groups. This phenomenon was first observed in p(DR1M-co-MMA) and p(DR1A-co-MMA) (Scheme 3) in comparison with a blend of pDR1A with pMMA. The photoinduced birefringence calculated per azobenzene group is much higher at very low azobenzene content in copolymers, suggesting that the isolated azobenzenes are much easier to move than the azobenzenes neighboring each other. In the blend, the photoinduced birefringence does not appear to depend on the azobenzene concentration, which means that neighboring groups influence each other mainly if they belong to the same polymer chain; the intrachain neighboring effect is negligible¹⁸. The thermal cis-trans isomerization rate appears also to depend on the presence of neighboring azobenzene groups²².

In liquid crystalline polymers (and in semicrystalline polymers) cooperative motion of this kind is very common and its cause is the steric effect of forming organized domains. To find out if in these amorphous polymers the steric effect is the dominant one, or if other effects are more important, a few copolymer series were synthesized, some of which are presented in Scheme 3.

Apart from this steric effect, a dipolar interaction is possible between these polar azobenzene groups. The methacrylates are mostly syndiotactic, as demonstrated by the proton and carbon NMR spectra²³. Electronic spectra show that the azobenzene groups tend to be antiparallel to each other in the random state, which means that orientation will reinforce this tendency. Thus, one would expect an antiparallel more stable arrangement of two neighboring azobenzene groups as shown in Figure 2.

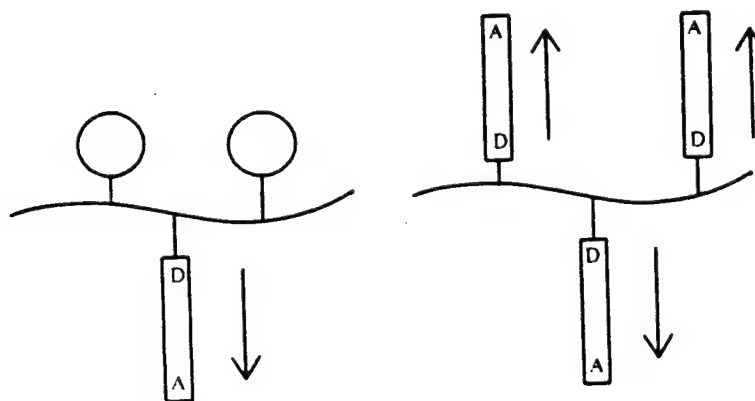


Figure 2. Arrangement of neighboring azobenzene groups.

If the dipolar factor is the dominant one in the cooperative motion of the azobenzene groups, then less polar groups should show a lesser degree of influence between neighbors. To test this hypothesis, p(DR1M-co-MEA) copolymers covering the whole range of compositions have been synthesized and their optical behavior investigated¹⁹. The results were not too conclusive, since here there are two types of azobenzene groups, reacting differently to the same laser wavelength. Overall, there seemed to be much less of cooperative motion in these copolymers than in p(DR1M-

co-MMA), but one cannot assign this to the lesser polarity of the MEA structural unit, since the same neighboring effect in DR1M units should be present here as well.

The answer to this question (dipolar or steric effect) can be given by analyzing the behavior of p(DR1M-co-BEM) and p(DR1M-co-NBEM) copolymer series (Scheme 3). These copolymers contain DR1M structural units, which generate photoinduced birefringence by repeated isomerization cycles, and "inert" structural units of the same shape, but very different polarities. The dipole moment of BEM is about 7D, similar to the dipole moment of DR1M²⁰, while the dipole moment of NBEM is close to 1D²¹. These two copolymer series behave entirely differently. In p(DR1M-co-BEM), there is an enhanced birefringence at low azobenzene contents, much more than in p(DR1M-co-MMA). This is due to the cooperative motion of the BEM structural units in concert with the DR1M units. Results obtained using polarized IR difference spectroscopy in Prof. M. Pérolet's laboratory at Laval University (Quebec, Canada) clearly show that the DR1M groups and the BEM groups move at different rates, and that BEM is being moved by the DR1M motion²⁴. Calculations using birefringence data²⁰ indicate that the BEM groups can produce as much as 80% of the birefringence obtained by the DR1M groups.

A very similar copolymer series, p(DR1M-co-NBEM) produces a linear dependence of the photoinduced birefringence on the azobenzene concentration²¹. This means that a sterically equivalent group (NBEM) does not move in concert with DR1M, and the only possible explanation is the absence of dipolar interactions between the two groups. Hence, it appears that the steric interaction which dominates liquid crystalline self-organization, plays a minor (if any) role in the cooperative motion of azobenzene and "inert" groups. The polarity of such groups is the dominant factor.

The thermodynamic tendency towards order. Most of the publications on photoinduced birefringence in azobenzene-containing polymers used liquid crystalline polymers. Since the liquid crystalline polymers have an intrinsic tendency to organize into oriented domains, the order parameter is much higher in such films, and so is the photoinduced birefringence. The main disadvantage of using a liquid crystalline (or semicrystalline) polymer is the propensity of these materials to conserve the order created (or facilitated) by light. Destroying this photoinduced orientation is not a trivial matter, hence "erasing" it (point C in Figure 1) is extremely difficult. Total erasure is actually impossible. We believe that the mechanism of erasure involves randomization of the orientation of various oriented domains, so that overall no order is perceived, while within each domain the liquid crystalline order is preserved.

Our studies have only included one semicrystalline polymer depicted in Scheme 2 (pDR19T)²⁵. Its degree of crystallinity is 16%, as determined by X-ray diffraction. The polymer forms amorphous films in which birefringence can be photoinduced at much higher levels than in the intrinsically amorphous polymer films (about three times higher). At the same time, however, the "written" spot forms its crystalline domains, and "erasing" becomes very difficult as explained above. One very interesting phenomenon is that the rigid groups present into the main chain participate in the alignment of the azobenzene groups, probably as part of the crystalline domains. This cooperative motion was also observed by infrared difference spectroscopy²⁵.

We plan to extend our studies to a variety of semicrystalline and liquid crystalline polymers.

Surface Gratings Inscription: Holographic Storage

If, instead of addressing one point on the surface of the polymer film with a laser beam, one creates an interference pattern, a holographic grating will be created in the polymer film, with regions of different refractive indices where the beams interact constructively or destructively. This is the basis of holographic storage, which makes extensive use of the whole film surface, thus affording a high density of data. There are quite a few reports of holographic storage especially in liquid crystalline polymer films (where the birefringence is higher than in amorphous films)²⁶⁻²⁸, but - at least in some cases - the diffraction efficiencies of such holographic gratings clearly exceed any efficiency which could be calculated with birefringence values of around 0.3 (typical for a liquid crystalline polymer).

While inscribing such holographic gratings on our amorphous polymers, it has become obvious that, with increasing the exposure time, the surface of the polymer was changing²⁹. A similar observation was reported by Tripathy et al³⁰. The surface grating depth depends on the laser exposure time and on the light polarization³¹, the best diffraction efficiency being obtained with circularly polarized light³². An atomic force microscopic profile of a surface after exposure to the laser is shown in Figure 3.

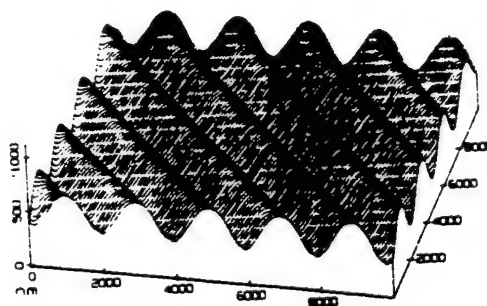


Figure 3. Surface of a polymer film after being subjected to a laser interfering pattern.

The mechanism of producing such a huge change in the surface of a polymer film below T_g (the heating induced by the laser is minimal, it has been calculated to be of the order of magnitude of a few degrees centigrade) is not yet clearly understood, although the presence of photoisomerizing azobenzene is essential. Such isomerization required free volume and may induce a pressure in the parts of the polymer film where there is high isomerization (circularly polarized light) and this may create a flow of the polymer towards the regions of low isomerization (where the interfering light is linearly polarized)³³. Clearly, more work is necessary in order to explain this completely unexpected and counterintuitive phenomenon. However, creation of such gratings and control of their depth and diffraction efficiencies are relatively easy to

achieve, thus one can envisage their use in photonics. We believe that at least some of the papers mentioned above as having reported volume gratings were actually dealing with surface gratings, based on the high diffraction efficiencies.

Surface holographic storage. The main difference between orienting the azobenzene groups and moving whole polymer molecules away from light (photoinduced birefringence and surface gratings inscription) is that the first process is optically reversible, i.e. the orientation can be locally randomized to its initial state by addressing with a circularly polarized light, while the surface gratings are "permanent", i.e. they cannot be optically erased. The only way to erase the grating is to heat the polymer film above its T_g , thus flattening the surface. New gratings can subsequently be inscribed on the surface. This is another argument in favor of the surface gratings interpretation in the previously published articles²⁶⁻²⁸. If these gratings were volume gratings (based on photoinduced birefringence), they would have been optically erasable, but the authors only mention erasing by heating above T_g .

The fact that inscribed surface gratings are not optically erasable can actually be exploited to increase the density of the holographic storage. Different gratings (i.e. having different orientations and/or different spacings) can be inscribed on the same film surface. We have inscribed, for example, eight gratings using only two directions at 90° to each other. The four gratings inscribed using the same direction differ by the spacing between the lines. These eight holograms can be identified separately, by looking at the each diffraction spot (Figure 4). Even more interesting, since the whole spectrum of an argon laser was used to inscribe these gratings, separate diffraction peaks can be read for the green and the blue wavelengths, which actually makes sixteen holograms inscribed in the same polymer film. Obviously, this is not an upper limit for storage, and it makes very little use of directional possibilities.

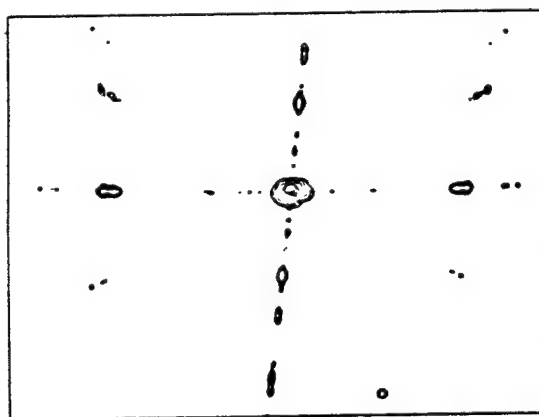


Figure 4. Diffractions of multiple holograms inscribed on a polymer film.

Coupling of light into and out of a film. Since the surface gratings are extremely efficient at directing the light into a diffracted direction, one can think of their use as points of coupling of lightwaves into and out of a film (typically into and out of a waveguide inscribed on a film). Experiments are being done in our laboratory to test

the efficiency of coupling and the losses within a waveguide laser-inscribed on a film of the azobenzene-containing polymer.

Two-beam coupling. Optical switching.

Using pCARBA¹⁵, and relying on previous reports of photorefractivity, such as poly(vinyl carbazole) films appropriately doped³⁴, or a stilbene-based NLO polymer³⁵, we wanted to test photorefractivity in our polymer films. The idea was that if the amino substituent on a stilbene group gives enough photoconductivity, then the carbazole group would be better. It is well known that all azobenzene-containing polymers can show electrooptic activity upon poling², and this property, coupled with the intrinsic photoconductivity of a carbazole-based polymer, should fulfill the conditions for the photorefractive effect³.

Photorefractive properties in a polymer generate a lot of possible uses in photonics, but from our point of view, the most interesting was the possibility to introduce an optical switch onto the polymer film. Having waveguides optically inscribed and erased (thus allowing changes after the patterns has been established) and having points of entry and exit created a basis for generating a whole photonic device on a polymer film by optical means. A switch would complete the possibilities, and a scheme of such a device is shown in Figure 5.

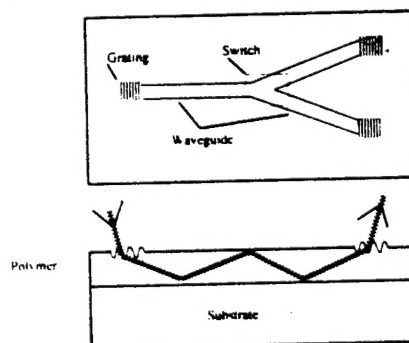
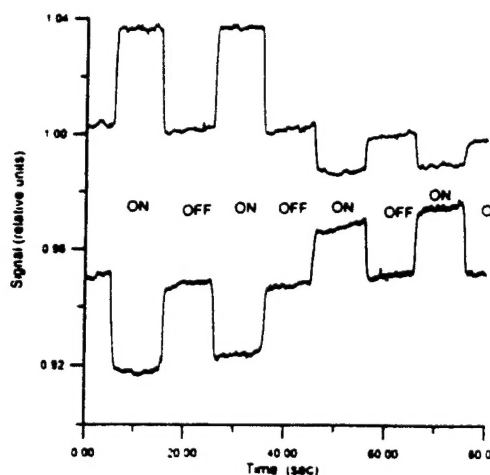


Figure 5. Photonic device optically inscribed on a polymer film.

On pCARBA, we have successfully obtained both asymmetric and symmetric two beam coupling, but the explanation is more complex than just the presence of the photorefractive effect. Typically, we use polarized light in the presence of an electric field to photo-pole the polymer film. High intensity interfering beams used for photoinduced poling also create volume and surface gratings, as described above. Such gratings diffract the light of the beams used for coupling, and symmetric two-beam coupling can actually be obtained in the absence of an electric field. A lot more work is needed to elucidate the phenomena contributing to these coupling effects. However, since asymmetric two beam coupling can be obtained, as demonstrated in Figure 6, in principle optical switching is possible, and a photonic "device" can be designed and operated.



Conclusions

The correlation between photoinduced birefringence levels, rates and efficiencies and the azobenzene polymer structure is well understood for amorphous polymers. The most intriguing structural aspect is the existence and the magnitude of a neighboring group effect. The arguments in favor of a dipolar mechanism governing this neighboring group effect are fairly convincing.

A more serious investigation is required in establishing the role of intrinsic order, or thermodynamic tendency to order, in the process of photoinducing birefringence.

The most exciting aspect of this research is the possibility to use these properties (photoinduced birefringence, surface gratings and two-beam coupling) in photonic devices design, given the simplicity of the material and of the necessary preliminary manipulation in order to obtain the desired effects.

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